Effect of composition, sonication and pressure on the rate capability of 5 V-$LiNi_{0.5}Mn_{1.5}O_4$ composite cathodes

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A B S T R A C T

Positive composite electrodes having $LiNi_{0.5}Mn_{1.5}O_4$ spinel as active material, a blend of graphite and carbon black for increasing the electrode electrical conductivity and either polyvinyldenefluoride (PVDF) or a blend of PVDF with a small amount of Teflon® (1 wt%) for building up the electrode. They have been processed by tape casting on an aluminum foil as current collector using the doctor blade technique. Additionally, the component blends were either sonicated or not, and the processed electrodes were compacted or not under subsequent cold pressing. Composites electrodes with high weight, up to 17 mg/cm^2, were prepared and studied as positive electrodes for lithium-ion batteries. The addition of Teflon® and the application of the sonication treatment lead to uniform electrodes that are well-adhered to the aluminum foil. Both parameters contribute to improve the capacity drained at high rates (5C). Additional compaction of the electrode/aluminum assemblies remarkably enhances the electrode rate capabilities. At 5C rate, remarkable capacity retentions between 80% and 90% are found for electrodes with weights in the range 3–17 mg/cm^2, having Teflon® in their formulation, prepared after sonication of their component blends and compacted under 2 tonnes/cm^2.

1. Introduction

Li-ion batteries (LIBs) are able to store high energy density. They also show long cycle life and are less pollutant that conventional rechargeable batteries [1–3]. These outstanding performances of LIBs make themselves the current technology for portable electronic devices (smartphones, laptop, tablets, etc.). Recently, LIBs have been chosen by most of the automakers as the power source for theirs hybrids and battery electric vehicles (EVs referred) [3,4]. A key factor for EVs is the battery, which must combine high energy and high power with low pollution and low cost.

The layered $LiCoO_2$ is the most used positive electrode (cathode referred) as active material in commercial LIBs [1,2,4]. However, its high cost, moderate thermal stability and environmental concern are severe problems for use in the large-size batteries needed for EVs [3,4]. Among the cathode materials proposed to replace the $LiCoO_2$, $LiMn_2O_4$-based oxides are ones of the best candidates due to their low cost and environment friendliness [1,2,4]. The $LiMn_2O_4$ oxide (LMS referred) has a cubic spinel structure, space group Fd-3m, in which the lithium ions are situated at the 8a tetrahedral positions, the manganese cations (Mn^{3+}, Mn^{4+}) at the 16d octahedral sites and the oxygen anions at the 32e octahedral positions. During the electrochemical charge/discharge processes the Li^+-ions are reversibly extracted/inserted from/into the spinel structure [5,6]. To improve the electrochemical performances of the LMS-based cathodes, doping with metallic cations has been the most followed strategy [7–10]. The $LiNi_{0.5}Mn_{1.5}O_4$ spinel (LNMS referred) is the most studied $LiMn_2O_4$-doped spinel [11–16] since Zhong et al. [11] showed that LNMS was able to de-/insert Li^+-ions at very high potential, ca. 4.7 V vs. Li^+/Li. Moreover, LNMS-based cathodes shows large reversible capacity (ca. 135 mAh/g) and remarkable rate capability [13,16]. Even they are able to store high specific energy (ca. 610 mWh/g), which is higher than that of $LiFePO_4$, undoped-$LiMn_2O_4$ and $LiCoO_2$. Because of these outstanding electrochemical performances the development of new LNMS-based electrodes is considered a hot topic in the battery field [4,15]. In fact, LNMS-based electrodes are cathode materials able to meet the performance/cost requirements needed for EVs.

The electrodes of LIBs are usually composites in which, besides the electrochemical active material (AM referred), other components are required in order to build up a film network with high electronic conductivity. The most usual conducting agent employed

to raise the electronic conductivity of the composite electrode is carbon black (CB) [9,13,17,18]. It has been demonstrated that the addition of other carbonaceous materials (graphite, graphene, carbon nanotubes, etc.) together with the CB allows improving the electrochemical performances of LIB-electrodes [19,20,21]. The composite electrodes must to have a percolating pore distribution through which the Li^+-ions of the electrolyte can fast move. To build this network, one or several polymeric additives are also included in the composite formulation. These binders notably improve the mechanical properties of the film [7,11,22,23] and the adherence of the electrode to the current collector. Poly(vinylidene fluoride) (PVDF), showing a high electrochemical stability on a wide potential window, is the most used binder in electrodes for LIBs [11,22,24]. It should be noted that the formulation of the composite electrode, besides the choice of the above indicated materials, involves the optimization of the mass and/or volume ratio. For instance, in previous papers some of us demonstrated that the capacity drained by electrodes using the $LiMn_2O_4$ spinel as AM, depended strongly on the AM/CB ratio [17,22]. To improve the specific energies (gravimetric and volumetric) of the composites electrodes, the content of the non-electroactive additives (conductive agents and binders) needs to be optimized [22,24].

Over the last five years, a number of papers have shown that the electrode processing is another key factor to manufacture high-energy and high-power electrodes for LIBs [4,19,24–27]. For a selected formulation of the composite electrode, its specific energy can be improved by engineering approaches such as the optimization of the porosity and/or the electrode thickness [28,29]. Moreover, the procedure used to blend the components of the composite electrode affects the homogeneity of the component distributions, and hence its electrochemical performances [30,31]. Thus, the search of the most influential parameters of the electrode processing is one of the most active topics in the LIB field.

This paper deals with the processing of $LiNi_{0.5}Mn_{1.5}O_4$-composite cathodes for LiBs. In particular, we have studied: (i) the electrode formulation, mainly the presence of a small content of Teflon®, (ii) the sonication treatment of the component blends, (iii) the compression pressure on the whole electrode/current collector, and (iv) the weight of the electrode per unit area of the current collector. The effect of these parameters on the rate capability of the processed cathodes has been analyzed and discussed in this work.

2. Experimental

Commercial $LiNi_{0.5}Mn_{1.5}O_4$ (LNMS), from Sigma–Aldrich, was chosen as cathode active material. A mixture of graphite (TIMREX SLX-50 from TIMCAL) and carbon black (super P from MMM) was used to raise the electrical conductivity of the composite electrode. Polyvinylidenefluoride (PVDF from Fluka) and Polytetrafluorethylene (Teflon® from Dupont) were chosen to build up the electrode, as well as to improve the electrode handling and adherence to the current collector. Two formulations for the composite electrode were studied:

A-Formulation (without Teflon®): 78 wt% $LiNi_{0.5}Mn_{1.5}O_4$; 7.5 wt% Carbon black; 2.5 wt% Graphite; 12 wt% PVDF

B-Formulation (with Teflon®): 78 wt% $LiNi_{0.5}Mn_{1.5}O_4$; 7.5 wt% Carbon black; 2.5 wt% Graphite; 11 wt% PVDF; 1 wt% Teflon®

In both cases, the components were mixed and dispersed in *N*-methylpyrrolidinone (NMP). $LiNi_{0.5}Mn_{1.5}O_4$ spinel (2 g) together with the other components in the mentioned percentages already set up was dispersed in 11 ml of NMP. In some particular cases, the mixture was sonicated (U referred) for 25 min and then stirred at room temperature for 48 h. In some others, the mixture was just stirred at room temperature for 48 h, i.e. without any sonication. Once we got homogeneous slurries, they were casted on aluminum foil (15 μm thickness) by the doctor blade technique. For most of composite cathodes, the blade height and speed were 850 μm and 10 mm/s, respectively. By this procedure we have got thick electrodes of ca. 120 cm^2 (10 cm × 12 cm) and ca. 14 mg/cm^2 (active material loading of ca. 11 mg/cm^2). To prepare electrodes with different active material loads, and hence with different thicknesses, the blade height was changed. Once the slurries were casted on the aluminum current collector, NMP was evaporated by heating at 80 °C on a hot plate for 2 h. Then, circular areas of the assembled electrode/current collector were cut with a punch holder of 12 mm in diameter. In some cases, these dried electrode/aluminum assemblies were additionally compacted under cold pressing of either 0.5 or 2 tonnes/cm^2 for 1 min. In all cases, the composite electrodes (formulations A or B) on aluminum foil were used as working electrodes in Li half-cells. The negative electrode was a lithium-metal foil, which also acted as reference electrode. The electrolyte was 1 M $LiPF_6$ solution in anhydrous ethylene carbonate and dimethyl carbonate (1:1 weight ratio). The two electrodes and the electrolyte, which was soaked in a Whatman BSF-80 glass, were assembled in coin-type cells (CR2032) within an argon glove box in which the water content was below 1 ppm. The cells were galvanostatically cycled by an Arbin instrument (model BT 2043) between 4 V and 5 V at C/5, C/2, 1C, 2C and 5C rates. These currents correspond to those expected for discharge times of 5, 2, 1, 0.5 and 0.2 h. The C-value is the capacity of the positive electrode calculated from the theoretical capacity of $LiNi_{0.5}Mn_{1.5}O_4$ (147 mAh/g) and the mass of this material in the composite electrode. The charge current was always C/2 except for the slowest tested rate for which C/5 was also used in the charge step. To analyze the effect of the discharge cut-off voltage on the capacity and energy of LNMS-cathodes, two selected electrodes, both of the B-formulation but one of them compacted under 2 tonnes/cm^2 and the other non-compacted were tested. The discharge curves were recorded for currents between C/5 and 5C, and the discharge cut-off voltage was progressively decreased from 4 V to 3.35 V on increasing current (0.14 mV for one C-unit).

3. Results and discussion

3.1. Electrode processing

$LiNi_{0.5}Mn_{1.5}O_4$ casted electrodes made up from the components defined for the A-formulation, i.e. without Teflon®, were deposited on Al current collector foil, and then heated at 80 °C till NMP evaporation. The component blend was not subjected to any sonication treatment. The casted electrode (Fig. 1a) looks rather uniform in spite that it was not subjected to any additional compaction. However, there are some small Al areas that were not covered by the electrode. The presence of these areas pointed out a deficient adherence of the composite electrode to the Al foil. The electrode of the B-formulation, i.e. with Teflon®, also prepared by the same procedure without any sonication treatment (Fig. 1b), shows some grains that were ascribed to Teflon®. The presence of these grains evidenced a deficient dispersion of Teflon® within the electrode. This electrode showed a good adherence to the Al foil. The electrode of the B-formulation in which its components were subjected to the sonication treatment is shown in Fig. 1c. The sonication treatment favors dispersion of the electrode components and the LNMS-electrode obtained looks more uniform. The electrode is well attached to the Al foil. Therefore, the presence of Teflon® favors a better adherence of the electrode to the Al foil and the sonication treatment favors a more uniform look of the electrode.

Another parameter studied in this work was the compaction of the LNMS-electrode/Al assemblies under a certain pressure. The dependence of the electrode thickness as a function of the blade height for electrodes of the B-formulation is shown in Fig. 2a.

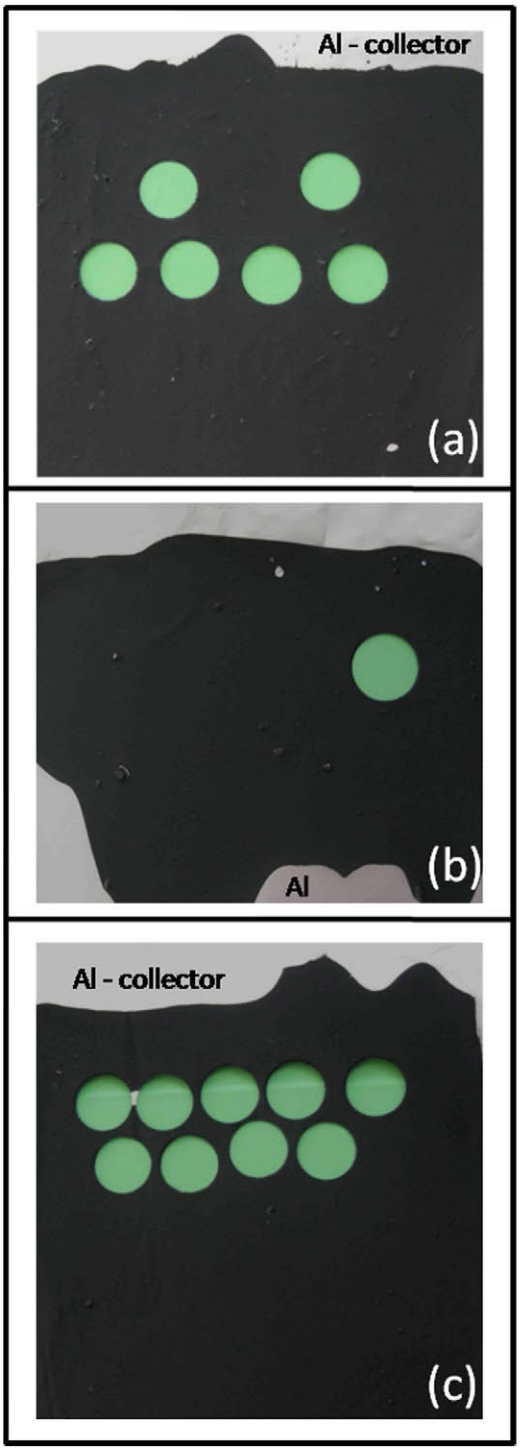

Fig. 1. Electrodes casted on aluminum foils by the doctor blade technique. (a) The electrode formulation was A (i.e. without Teflon®) and the component blend was sonicated. (b) The electrode formulation was B (i.e. with Teflon®) and the component blend was not sonicated. (c) The electrode formulation was B and the component blend was sonicated. For the three composite electrodes, no additional pressure for compaction was applied. The holes correspond to the circular electrodes (12 mm in diameter) cut to perform the electrochemical test.

This figure compares the electrode thickness of the non-compacted electrodes with that of the 2 tonnes/cm^2 compacted ones. In both cases, the electrode thickness was determined by subtracting the thickness of the Al current collector (15 μm) from the thickness of the complete electrode/Al assemblies. Data in Fig. 2a clearly show that the electrode thickness increases linearly as a function

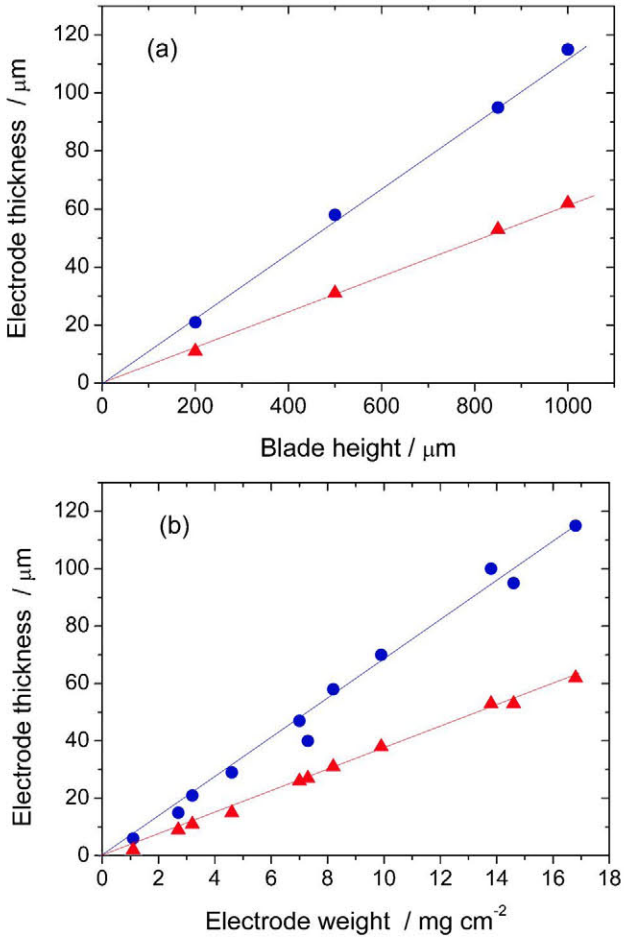

Fig. 2. (a) Variation of electrode thickness vs. blade height and (b) vs. electrode weight. Circles and triangles stand for the non-compacted electrodes and the 2 tonnes/cm^2-compacted ones, respectively. Straight lines are the best fits to the experimental data.

of the blade height. The slope is of 0.116 for the non-compacted electrodes (circles) and 0.064 for the compacted electrodes (triangles). The lower electrode thickness found after compaction, which can be explained by air removal, is a remarkable technological advantage because the same electrode weight occupies less volume. The variation of the electrode thickness as a function of the electrode weight, the latter normalized by the geometrical area, is shown in Fig. 2b. Linear dependences are observed for both non-compacted electrodes (circles) and compacted ones (triangles) up to the highest electrode weight of 17 mg/cm^2 (active material loading = 17 × 0.78 mg/cm^2). The linear dependences found indicate that the microstructure of the composite electrodes is maintained as the loading increases. Processing methods for which a linear evolution of thickness vs. electrode weight is followed are useful to manufacture composite electrodes with capacity values adapted to specific applications. The slope for the compacted electrodes (3.71 μm cm^2/mg) is lower than that for the non-compacted ones (6.8 μm cm^2/mg). The lower thickness found for the compacted electrodes points out a reduction of ca. 50% by volume while keeping the same electrode weight. Tran et al. [19] reported a near linear raise of the active material loading vs. electrode thickness up to 8 mg/cm^2 for composite cathodes of layered $LiNi_{0.87}Co_{0.15}Al_{0.05}O_2$. In our case, the lineal region is extended to 17 mg/cm^2.

Taking into account the mass and density of each component within the composite electrode, it was possible to calculate the theoretical electrode volume ($V_{calc.}$). Then, the electrode porosity in percent was calculated according to the equation: Porosity

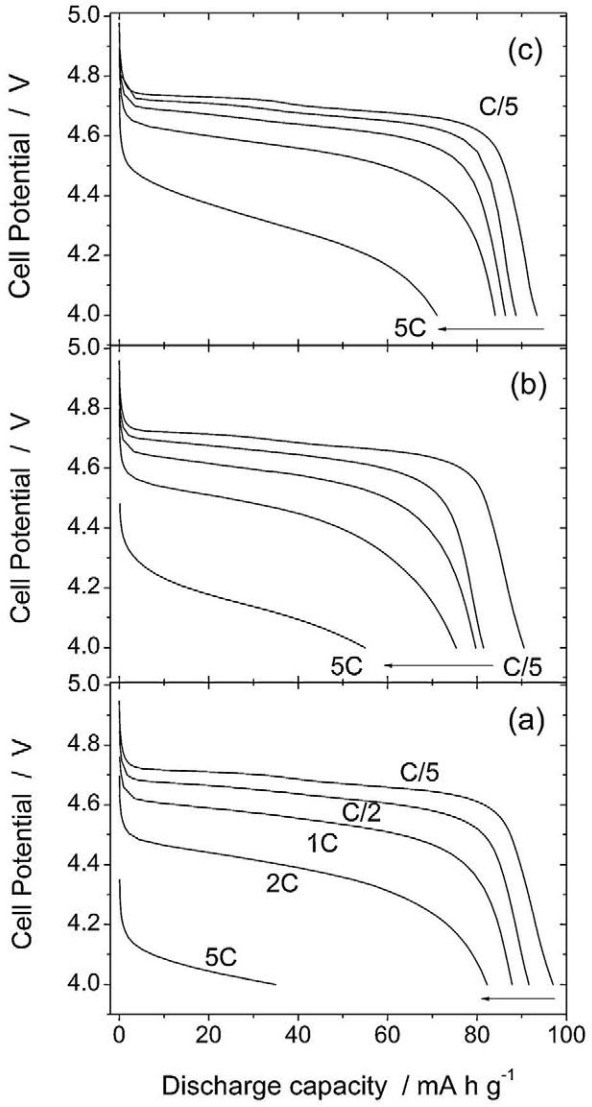

Fig. 3. Discharge galvanostatic profiles recorded at C/5, C/2, 1C, 2C and 5C rates for the electrodes of the B-formulation with 14 mg/cm^2 weight that were compacted at several pressures. (a) Non-compacted electrode, (b) electrode compacted at 0.5 tonnes/cm^2, and (c) electrode compacted at 2 tonnes/cm^2. In the three cases the electrode blends were sonicated.

(%) = $(V_{exp.} - V_{calc.}) \times 100/V_{exp.}$. The value of $V_{exp.}$ was determined from the circular surface area and the thickness of the tested electrode. Despite the large number of electrodes that have been processed in this work (Fig. 2b), the electrode porosity was ca. 60% for all the non-compacted electrodes and ca. 25% for all the 2 tonnes/cm^2 compacted ones. It is important to note that the low porosity is an advantage from the point of view of saving electrode space, but certain porosity is necessary to allow the access of the electrolyte Li^+ ions to the active electrode material [28], i.e. to $LiNi_{0.5}Mn_{1.5}O_4$ in this work.

3.2. *Rate capability studies*

Fig. 3 shows the discharge galvanostatic plots obtained at certain currents, between C/5 and 5C, for the non-compacted (Fig. 3a) and compacted electrode/Al assemblies, either at 0.5 tonnes/cm^2 (Fig. 3b) or at 2 tonnes/cm^2 (Fig. 3c). In all cases, the electrode formulation was that called B, the blends of the electrode components were sonicated, and the electrode weight was high (14 mg/cm^2). As already discussed, the compaction process allowed decreasing the electrode thickness from 128 μm, 84 μm and 60 μm for the non-compacted, 0.5 tonnes/cm^2 and 2 tonnes/cm^2 compacted, respectively. The porosity also decreased from 60%, to 37% and 22%, respectively. For the three cases, the discharge capacity was measured at the cut-off voltage of 4.0 V. At the lowest tested rate (C/5), similar curves are observed for the three B-electrodes independent of the compaction pressure applied. The profiles show two plateaus associated with reduction from Ni^{4+} to Ni^{3+} and from Ni^{3+} to Ni^{2+} [11,14,32]. The measured discharge capacity, ca. 95 mAh/g, is lower than the theoretical discharge one (147 mAh/g for $LiNi_{0.5}Mn_{1.5}O_4$), and smaller than the experimental capacities (110–130 mAh/g) reported for LNMS-samples synthesized by different procedures [11,15,33]. The moderate values of capacity found can be explained by the presence of non-active impurities in the LNMS-commercial sample as well as by the high cut-off discharge voltage chosen (4.0 V). On increasing the rate (>C/5), the two-discharge plateaus are not clearly distinguished, and the whole plateau profile becomes the more and more sloped. Taking the average voltage of the whole plateau ($E_{av.}$) as the parameter to characterize it, for the three electrodes, $E_{av.}$ decreases as the discharge current increases. However, the decrease of $E_{av.}$ vs. the rate is different for every cathode. At the lowest rate of C/5, E_{av} is ca. 4.7 V for the three electrodes, the non-compacted electrode and the two compacted ones. At 2C rate, the average voltage is 4.39 V for the non-compacted electrode (60% of porosity), 4.45 V for the 0.5 tonnes/cm^2 compacted electrode (37% of porosity) and 4.56 V for the 2 tonnes/cm^2 compacted one (22% of porosity). The higher E_{av}-value found for the 2 tonnes/cm^2 compacted electrode, which has the lowest porosity, evidences a lower internal resistance of the cell, which can be associated with a lower resistance of the composite electrode. These results show the positive effect of the electrode compaction on the average voltage, mainly at high currents. Fongy et al. [28] reported a decrease of the potential plateau for $LiFePO_4$ cathodes on increasing the porosity. This behavior was associated with electronic limitations caused by the lower compaction of the electrode. To analyze the effect of the electrode compaction on the LNMS-discharge capacity, the variation of the normalized capacity (Q_{nor}) vs. current is shown in Fig. 4a. At rates below 2C, the Q_{nor}-values are nearly the same for the non-compacted and compacted electrodes. However at the 5C rate, the discharge capacity was only 36% of the capacity measured at C/5 for the non-compacted electrode, 61% for the 0.5 tonnes/cm^2 compacted electrode and 75% for the 2 tonnes/cm^2 compacted one. These results evidence the benefit effect of the electrode compaction on the electrode capacity, mainly if the electrodes are thought to work at high currents.

Because the studies of the rate capability do not establish whether the cut-off voltage ($E_{cut\text{-}off}$) must be kept constant or must be decreased as the discharge current increases, we have also measured the capacity of two electrodes progressively changing the discharge $E_{cut\text{-}off}$ from 4 to 3.35 V. Fig. 4b shows the dependence of the normalized discharge capacity as a function of the current for the non-compacted electrode and 2 tonnes/cm^2 compacted one. As expected, the normalized capacity shows values different from those shown in Fig. 4a for these electrodes. The normalized capacity decreases as the current increases being the decrease more pronounced for the non-compacted electrode. Therefore, Fig. 4a and b show the same physical meaning with independence of the $E_{cut\text{-}off}$ chosen. Here-after the discharge cut-off voltage taken was 4 V for all currents.

Fig. 4b also shows the dependence of the normalized specific energy as a function of the current. The specific energy is an important electrochemical parameter because it involves the capacity and the average working voltage. Hence, its variation as a function of the current includes the variations of both parameters. As the current increases, the normalized specific energy decreases for the non-compacted and 2 tonnes/cm^2 compacted electrode. The

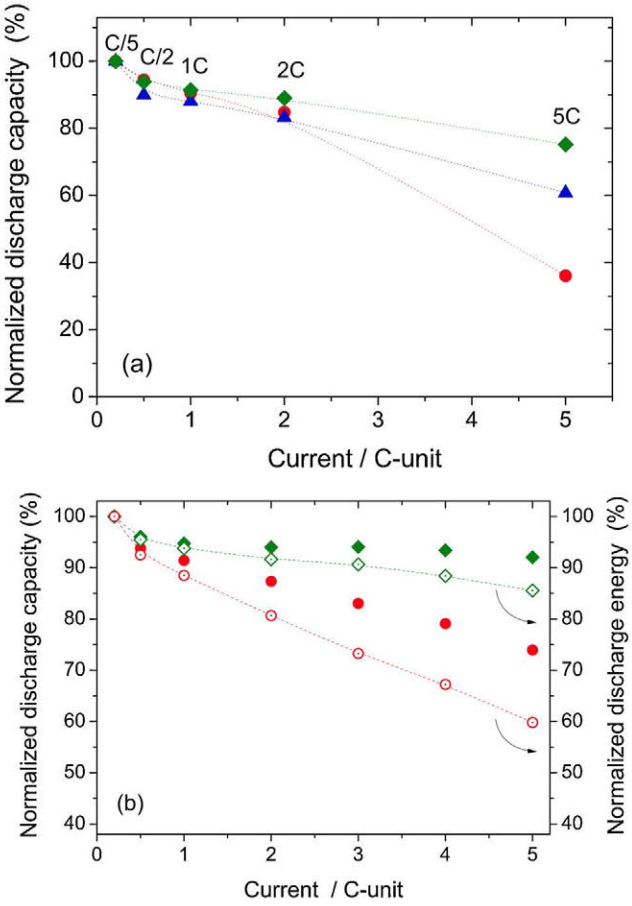

Fig. 4. (a) Normalized discharge capacity vs. current for the non-compacted electrode (circles), the 0.5 tonnes/cm^2-compacted electrode (triangles) and the 2 tonnes/cm^2-compacted one (diamond). The three electrodes had the same formulation (B) and weight (14 mg/cm^2), and the component blends had been sonicated. The cut-off voltage was 4 V (1C = 147 mA/g). (b) Normalized discharge capacity and normalized energy density vs. current. Circles and diamonds stand for the non-compacted electrode and 2 tonnes/cm^2-compacted one, respectively. The discharge cut-off voltage was progressively decreased from 4 V to 3.35 V on increasing the current.

normalized specific energy is lower for the non-compacted electrode, especially at high currents (≥2C). Moreover, at a given current and especially at high currents, the normalized specific energy shows notably lower values compared to the normalized capacity. It is a consequence of the decrease in the average voltage plateau.

Tran et al. [19] also found an improvement of the rate capability of the layered $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$-cathodes when the compaction pressure was raised from 0 to 6 tonnes/cm^2. Therefore, the results obtained for the three most used families of cathodes in commercial LIBs, i.e. layered $LiCoO_2$ [19], $LiMn_2O_4$ based-spinels (present paper) and olivine $LiFePO_4$-based compounds [28], point out that electrode compaction is a key factor to improve the electrochemical performances, especially for demanding high currents.

The effect of the electrode weight, expressed in weight per unit area (mg/cm^2) on the rate capability is analyzed in Fig. 5. All the electrodes had the same B-formulation, the component blends were subjected to the same sonication treatment, and the electrode/Al assemblies were compacted at the same pressure, 2 tonnes/cm^2. The total electrode weight (without collector) varied from 2.7 mg/cm^2 (diamonds), to 7.3 mg/cm^2 (triangles) and to 16.8 mg/cm^2 (circles). For the three electrodes, the normalized discharge capacity decreases slightly as the current increases from C/5 (30 mA/g) to 5C (735 mA/g). The decrease is more pronounced for

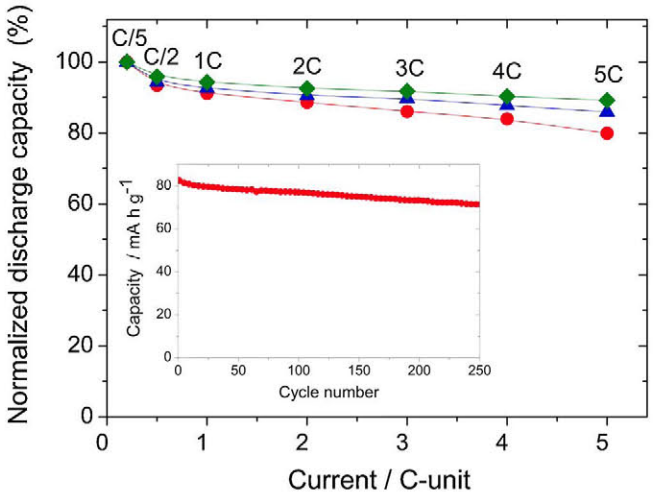

Fig. 5. Normalized discharge capacity vs. current for electrodes having several weights: 2.7 mg/cm^2 (diamonds), 7.3 mg/cm^2 (triangles) and 16.8 mg/cm^2 (circles). The three electrodes have the B-formulation, the same sonication treatment and they were compacted under the same pressure (2 tonnes/cm^2). The inset shows the long-cycling behavior of 16.8 mg/cm^2 electrode (circles). The voltage region explored was: 4–5 V and 1C = 147 mA/g.

the heaviest electrode, but even in this case the capacity retention is as high as 80% at 5C rate. This result points out high capacity retention of $LiNi_{0.5}Mn_{1.5}O_4$ spinel even if the electrode weight increases up to 16.8 mg/cm^2. Despite the increase of the electrode weight by ca. 7 times, the decrease of the discharge capacity at 5C was only 10% (Fig. 5), from 90% for the electrode of 2.7 mg/cm^2 (9 μm thickness) to 80% for the electrode of 16.8 mg/cm^2 (62 μm thickness). This is a remarkable result that shows it is possible to prepare $LiNi_{0.5}Mn_{1.5}O_4$ composite cathodes with energy (in Wh/cm^2) increasing by ca. seven times while keeping nearly the same specific energy (in Wh/kg). That is, almost the same percentage of active material works for the thickest electrode processed (16.8 mg/cm^2 and 62 μm). For this electrode, the long-term cyclability was tested at 1C charge/discharge rate from 4 V to 5 V. After 250 cycles, the capacity retention was 86.6% (inset in Fig. 5). This result shows the high cycleability of this electrode.

Fig. 6 shows the variation of the normalized discharge capacity as a function of the current for two electrodes having the same B-formulation, the same weight (14 mg/cm^2), and compacted at the

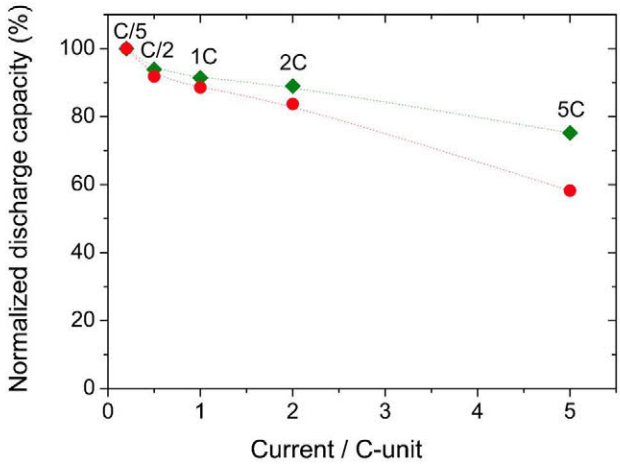

Fig. 6. Normalized discharge capacity vs. current for electrodes of the same B-formulation, same weight (14 mg/cm^2) and same compaction pressure (2 tonnes/cm^2) but with the component blend either sonicated (diamonds) or not (circles). The voltage region explored was from 4 V to 5 V and 1C = 147 mA/g.

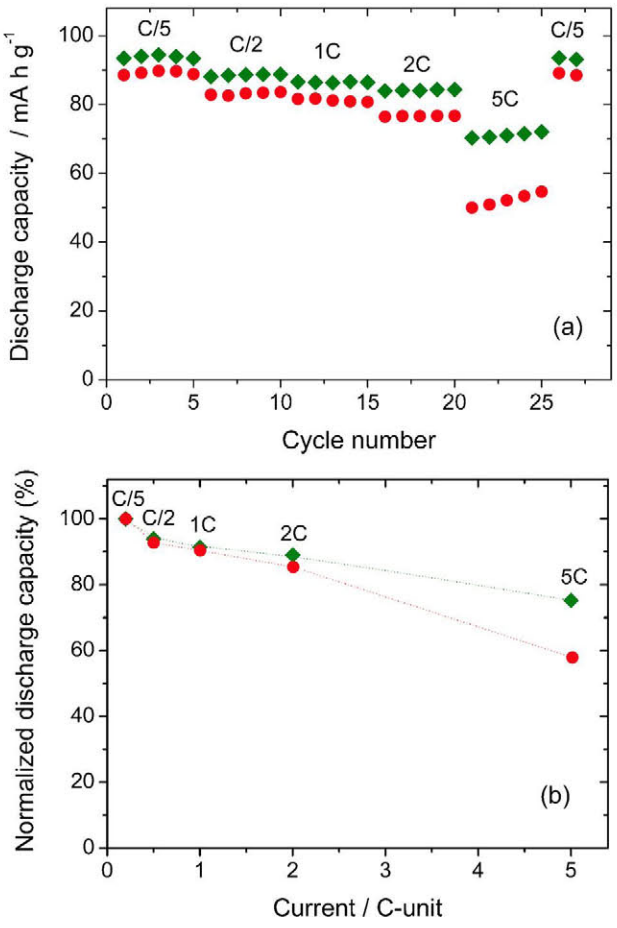

Fig. 7. (a) Discharge capacity registered at several rates vs. cycle number for electrodes of formulations: A (without Teflon®, circles) and B (with Teflon®, diamonds). (b) Normalized discharge capacity vs. current for the electrodes of formulations: A (circles) and B (diamonds). The two electrodes have the same weight (14 mg/cm^2), their component blends were sonicated, and the two electrodes were compacted at 2 tonnes/cm^2. (Voltage region: 4–5 V, 1C = 147 mA/g).

same pressure (2 tonnes/cm^2). However, in one case, the component blend was sonicated (diamonds) and in the other case not (circles). The two electrodes show nearly the same normalized discharge capacity for currents below 2C rate, 89% and 84% for the sonicated blend and non-sonicated one at 2C, respectively. However, at 5C the electrode in which the blend was sonicated shows a higher normalized discharge capacity, 75% against 58%. Therefore, sonication of the component blends has a beneficial effect for electrodes thought to work at rates above 2C. Ponrouch and Palacín [31] reported the improvement of the electrochemical performances of composite anodes of MCMB-graphite or Co_3O_4 when a sonication treatment was used to process the electrodes. The improvement was explained because sonication promotes the homogeneity of the composite preserving the structure of the active electrode materials. In our case, a better homogeneity of the B-formulation composite electrodes was observed (Fig. 1c).

Finally, the effect of the presence of Teflon® on the rate capability is analyzed in Fig. 7. The electrodes were of the A or B-formulations, i.e. without or with Teflon®, and had the same weight (14 mg/cm^2). Their component blends were subjected to the same sonication treatment and the electrode/Al assemblies were compacted under the same pressure, 2 tonnes/cm^2. Fig. 7a shows that the discharge capacity is rather similar for the two electrodes with the exception of the values measured at the 5C rate. It should be noted that no appreciable differences in capacity are observed for the five cycles measured at each rate. This result shows a good cycleability of the $LiNi_{0.5}Mn_{1.5}O_4$ composite cathode at all the currents tested. Moreover, the recovery of the discharge capacity at C/5, after the rate capability study, clearly proves that the capacity fade observed on increasing the current is only due to kinetic causes. To better compare the influence of Teflon® on the rate capability, the normalized discharge capacity registered at the 3rd cycle of each rate is plotted vs. the current in Fig. 7b. The discharge capacities measured up to 2C rate is high (>85%) and nearly the same for the two electrodes. Only at the 5C rate, the normalized capacity is higher for the composite cathode having Teflon®, 75% against 57%. Therefore, the presence of Teflon® leads to a higher discharge capacity at high rates. This is a serendipity result because a low content of Teflon® of 1 wt% leads to an improvement of the rate capability.

4. Conclusions

$LiNi_{0.5}Mn_{1.5}O_4$ composite cathodes having a blend of graphite and carbon black to improve the electrode electrical conductivity, and PVDF or a blend of PVDF plus Teflon® to build up the electrode have been processed by the doctor blade technique on Al foil current collector. Sonication of the component blends in *N*-methylpyrrolidinone on the one hand, and the presence of a small amount of Teflon® (1 wt%) added to the main binder PVDF (11 wt%) on the other, contribute to get more uniform electrodes and well-adhered electrodes to the Al-current collectors. Compaction of the electrode/Al assemblies under cold pressure leads to: (i) a decrease of the electrode thickness, which is more important as the electrode weight increases, and (ii) a decrease of the electrode porosity, from ca. 60% for all the non-compacted electrodes to ca. 25% for the 2 tonnes/cm^2 compacted ones. A linear increase of the electrode thickness with the weight of the composite electrode has been found in both non-compacted and 2 tonnes/cm^2 compacted composite cathodes up to values as high as 17 mg/cm^2.

The influence of several processing parameters (compaction, electrode formulation and sonication) on the rate capability of thick $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathodes has been studied. Despite the high electrode weight (ca. 14 mg/cm^2), the electrodes exhibit elevate rate capability with capacity retentions higher than 80% at 2C rate. Sonication of the blends and the presence of Teflon® have a moderate effect on the rate capability of the composite electrodes. Only at very high rate (5C) an increase in the discharge capacity is observed for the electrodes obtained after sonication and having Teflon® in their formulation. Compaction of the electrode/Al assemblies has a more important effect on the rate capability, mainly at high currents. At 5C, the normalized discharge capacity increases from 36% for the non–compacted electrodes (60% of porosity) to 61% for the 0.5 tonnes/cm^2-compacted electrodes (37% of porosity) and to 75% for the 2 tonnes/cm^2 compacted ones (22% of porosity). This result shows that electronic limitations can be overcome through electrode compaction. In summary, electrodes having 1 wt% Teflon® in their formulation, their component blends subjected to a sonication treatment, compacted at 2 tonnes/cm^2 and with weights in the range 2.7–17 mg/cm^2 showed a remarkable rate capability. Even at the high current of 5C, the normalized discharge capacity was between 80% and 90% for all these electrodes.

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References

[1] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature 414 (2001) 359–367.

[2] M.R. Palacín, Recent advances in rechargeable battery materials: a chemist's perspective, Chemical Society Review 38 (2009) 2565–2575.

[3] B.G. Pollet, I. Staffell, J.L. Shang, Current status of hybrid, battery and fuel cell electric vehicles: from electrochemistry to market prospects, Electrochimica Acta 84 (2012) 235–249.

[4] T.-H. Kim, J.S. Park, S.K. Chang, S. Choi, J.H. Ryu, H.-K. Song, The current move of lithium ion batteries towards the next phase, Advanced Energy Materials 2 (2012) 860–872.

[5] M.M. Thackeray, P.J. Johnson, L.A. de Picciotto, P.G. Bruce, J.B. Goodenough, Electrochemical extraction of lithium from $LiMn_2O_4$, Materials Research Bulletin 19 (1984) 179–187.

[6] M.A. Monge, J.M. Amarilla, E. Gutierrez-Puebla, J.A. Campa, I. Rasines, Atomic level study of $LiMn_2O_4$ as electrode in lithium batteries, ChemPhysChem 4 (2002) 367–370.

[7] L. Guohua, H. Ikuta, T. Uchida, M. Wakihara, The spinel phases $LiM_yMn_{2-y}O_4$ (M = Co, Cr, Ni) as the cathode for rechargeable lithium batteries, Journal of the Electrochemical Society 143 (1996) 178–182.

[8] R.M. Rojas, J.M. Amarilla, L. Pascual, J.M. Rojo, D. Kovacheva, K. Petrov, Combustion synthesis of nanocrystalline $LiNi_YCo_{1-2Y}Mn_{1+Y}O_4$ spinels for 5 V cathode materials. Characterization and electrochemical properties, Journal of Power Sources 160 (2006) 529–535.

[9] J.M. Amarilla, K. Petrov, F. Picó, G. Avdeev, J.M. Rojo, R.M. Rojas, Sucrose-aided combustion synthesis of nanosized $LiMn_{1.99-y}Li_yM_{0.01}O_4$ ($M = Al^{3+}$, Ni^{2+}, Cr^{3+}, Co^{3+}, $y = 0.01$ and 0.06) spinels. Characterization and electrochemical behavior at 25 and at 55 °C in rechargeable lithium cells, Journal of Power Sources 191 (2009) 591–600.

[10] M. Prabu, M.V. Reddy, S. Selvasekarapandian, G.V. Subba Rao, B.V.R. Chowdari, (Li, Al)-co-doped spinel, $Li(Li_{0.1}Al_{0.1}Mn_{1.8})O_4$ as high performance cathode for lithium ion batteries, Electrochimica Acta 88 (15) (2013) 745–755.

[11] Q. Zhong, A. Bonakclarpour, M. Zhang, Y. Gao, J.R. Dahn, Synthesis and electrochemistry of $LiNi_xMn_{2-x}O_4$, Journal of the Electrochemical Society 144 (1997) 205–213.

[12] K. Ariyoshi, Y. Iwakoshi, N. Nakayama, T. Ohzuku, Topotactic two-phase reactions of $Li[Ni_{1/2}Mn_{3/2}]O_4$ (P_{4332}) in non aqueous lithium cells, Journal of the Electrochemical Society 151 (2004) A296–A303.

[13] J.C. Arrebola, A. Caballero, M. Cruz, L. Hernán, J. Morales, E. Rodríguez Castellón, Crystallinity control of a nanostructured $LiNi_{0.5}Mn_{1.5}O_4$ spinel via polymer-assisted synthesis: A method for improving its rate capability and performance in 5 V lithium batteries, Advanced Functional Materials 16 (2006) 1904–1912.

[14] M. Aklalouch, J.M. Amarilla, R.M. Rojas, I. Saadoune, J.M. Rojo, Chromium doping as a new approach to improve the cycling performance at high temperature of 5 V $LiNi_{0.5}Mn_{1.5}O_4$-based positive electrode, Journal of Power Sources 185 (2008) 501–511.

[15] G.Q. Liu, L. Wen, Y.M. Liu, Spinel $LiNi_{0.5}Mn_{1.5}O_4$ and its derivatives as cathodes for high-voltage Li-ion batteries, Journal of Solid State Electrochemistry 14 (2010) 2191–2202.

[16] M. Aklalouch, J.M. Amarilla, I. Saadoune, J.M. Rojo, $LiCr_{0.2}Ni_{0.4}Mn_{1.4}O_4$ spinels exhibiting huge rate capability at 25 and 55 (C: Analysis of the effect of the particle size, Journal of Power Sources 196 (2011) 10222–10227.

[17] S. Mandal, J.M. Amarilla, J. Ibáñez, J.M. Rojo, The role of carbon black in $LiMn_2O_4$-based composites as cathodes for rechargeable lithium batteries, Journal of the Electrochemical Society 148 (2001) A24–A29.

[18] K. Maher, K. Edström, I. Saadoune, T. Gustafsson, M. Mansori, Synthesis and characterization of carbon-coated $Li_{0.5}Ni_{0.25}TiOPO_4$ anode material, Electrochimica Acta 54 (2009) 5531–5536.

[19] H.Y. Tran, G. Greco, C. Täubert, M. Wohlfahrt-Mehrens, W. Haselrieder, A. Kwade, Influence of electrode preparation on the electrochemical performance of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ composite electrodes for lithium-ion batteries, Journal of Power Sources 210 (2012) 276–285.

[20] A. Ponrouch, M.R. Palacín, Optimisation of performance through electrode formulation in conversion materials for lithium ion batteries: Co_3O_4 as a case example, Journal of Power Sources 212 (2012) 233–246.

[21] Z.S. Wu, G. Zhou, L.C. Yin, W. Ren, F. Li, H.M. Cheng, Graphene/metal oxide composite electrode materials for energy storage, Nano Energy 1 (2012) 107–131.

[22] M.G. Lazarraga, S. Mandal, J. Ibañez, J.M. Amarilla, J.M. Rojo, $LiMn_2O_4$-based composites processed by a chemical-route microstructural, electrical, electrochemical, and mechanical characterization, Journal of Power Sources 115 (2003) 315–322.

[23] J. Chong, S. Xun, H. Zheng, X. Song, G. Liu, P. Ridgway, J.Q. Wang, V.S. Battaglia, A comparative study of polyacrylic acid and poly(vinylidene difluoride) binders for spherical natural graphite/$LiFePO_4$ electrodes and cells, Journal of Power Sources 196 (2011) 7707–7714.

[24] J. Li, C. Daniel, D. Wood, Materials processing for lithium-ion batteries, Journal of Power Sources 196 (2011) 2452–2460.

[25] B. Lestriez, Functions of polymers in composite electrodes of lithium ion batteries, C. R. Chimie 13 (2010) 1341–1350.

[26] Y.H. Chen, C.W. Wang, X. Zhang, A.M. Sastry, Porous cathode optimization for lithium cells: ionic and electronic conductivity, capacity, and selection of materials, Journal of Power Sources 195 (2012) 2851–2862.

[27] G. Liu, H. Zheng, X. Song, V.S. Battaglia, Particles and polymer binder interaction: a controlling factor in Lithium-Ion electrode performance, Journal of the Electrochemical Society 159 (2012) A214–A221.

[28] C. Fongy, A.C. Gaillot, S. Jouanneau, D. Guyomard, B. Lestriez, Ionic vs electronic power limitations and analysis of the fraction of wired grains in $LiFePO_4$ composite electrodes, Journal of the Electrochemical Society 157 (2010) A885–A891.

[29] H. Zheng, J. Li, X. Song, G. Liu, V.S. Battaglia, A comprehensive understanding of electrode thickness effects on the electrochemical performances of Li-ion battery cathodes, Electrochimica Acta 71 (2012) 258–265.

[30] K.M. Kim, W.S. Jeon, I.J. Chung, S.H. Chang, Effect of mixing sequences on the electrode characteristics of lithium-ion rechargeable batteries, Journal of Power Sources 83 (1999) 108–111.

[31] A. Ponrouch, M.R. Palacín, On the impact of the slurry mixing procedure in the electrochemical performance of composite electrodes for Li-ion batteries: a case study for mesocarbon microbeads (MCMB) graphite and Co_3O_4, Journal of Power Sources 196 (2011) 9682–9688.

[32] Y. Terada, K. Yasaka, F. Nishikawa, T. Konishi, M. Yoshio, I. Nakai, In situ XAFS analysis of $Li(Mn,M)_2O_4$ (M = Cr, Co, Ni) 5 V cathode materials for lithium-ion secondary batteries, Journal of Solid State Chemistry 156 (2001) 286–291.

[33] J.M. Amarilla, R.M. Rojas, J.M. Rojo, Understanding the sucrose-assisted combustion method: effects of the atmosphere and fuel amount on the synthesis and electrochemical performances of $LiNi_{0.5}Mn_{1.5}O_4$ spinel, Journal of Power Sources 196 (2011) 5951–5959.